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## *THE CONTINUOUS ADVANCE OF ELECTROCHEMISTRY.*

THE field of electrochemical activity covers three distinct lines of endeavor: First, the investigation and classification of electrochemical phenomena—scientific progress; second, the formulation of a satisfactory and all-comprehensive electrochemical theory—intellectual progress; and third, the application of these facts to industrial ends—industrial progress. We purpose to discuss briefly this evening the past achievements in each of these lines of endeavor, in order to determine therefrom and to discuss more at length the present bent and probable future direction and extension of each.

### I. THE INVESTIGATION AND CLASSIFICATION OF ELECTROCHEMICAL PHENOMENA.

This is, properly speaking, the real corner-stone of progress in electrochemical science. What has been accomplished in this direction in the century and a half since Beccaria 'revivified' several metals by Leyden-jar discharges may be found scattered through the files of our technical journals and compiled from time to time into compendiums of electrochemical literature. The most pretentious, and in many respects the most timely, of all these works is the 'ausführliches Handbuch,' which our German friends are at present patiently compiling. A careful study of this work causes surprise both at the large amount of investigation which has been done and at the large gaps which exist in our experimental knowledge. Alongside of splendid researches into the most obscure phenomena of the science exist *lacunæ* in

our knowledge of some of the simplest electrochemical phenomena, such as, for instance, in the facts concerning the simultaneous deposition of two or more metals from solution. While doing this the impression grows strong upon us that electrochemistry has lost much because of a lack of cooperation among electrochemical investigators, and because of the desultory, haphazard manner in which their efforts have been frequently applied.

The lack of a coordinating, directing, systematizing influence among electrochemical workers has been the crying need of the science, and it is just this influence, above all things, which is furnished by our electrochemical societies. The Bunsen Society in Germany, the Faraday Society in England, our own society in America have brought electrochemists together, making them acquainted with each other's work, and in particular with the need of experimental work along neglected lines, and have thus furnished the coordinating agency until recently so deplorably lacking.

Davy and Faraday laid broad the experimental foundations of this science by the electrolytic decomposition of many of our most common chemical compounds. Bunsen supplemented this by attacking the rarer metals. Kohlrausch investigated specific conductivities of almost numberless solutions. Beetz and Lorenz fused salts; Moissan the electrochemistry of high temperatures; Hittorf and Ostwald and Nernst the mechanism of electrolysis of solutions, while in between these monumental investigations hundreds of others have contributed to the advance. But still if the army of investigators, as regards numbers, had been in reality an army as regards organization and systematically directed effort, how much more valuable would its work have been! Is it not a fact that one of the results of our semi-annual meetings is that we learn and have impressed upon us the gaps in experimental electrochemistry, and that we often, either deliberately or tacitly, divide the work among us for systematic investigation?

Let me indicate some of the many electrochemical subjects which need systematic attack and orderly study. The electric conductivity of some common salts is as yet undetermined, not to mention most of the rarer ones. Braun, Graetz and Poincairé did good work on the conductivity of fused salts many years ago, but for every salt they tested there are a dozen or a score awaiting investigation. The results of the electrolysis of solutions of different salts, of different concentrations, at different temperatures, with differing electrodes and current densities, has been merely touched here and there; the great body of that information is ripe for harvest to whoever can wield the sickle. The study of the electrolysis of fused salts, or of solutions of chemical compounds dissolved in fused baths, is scarcely begun. One can go into the laboratory any afternoon and start an electrochemical study of a salt which has never before been taken up, and there are enough such to keep the laboratory busy a long, long time.

The use of accurately controlled electrodeposition for the purpose of determining the chemical equivalents of the metals is a method which has not received the attention which it deserves. It is quite certain that the atomic weights of many elements, whose exact value is at present uncertain, could be fixed satisfactorily in this manner. The calorimetric investigation of electrolytic cells in operation, inaugurated by Faure, is an attractive field wide open for the experimenter, and from which much valuable information could be drawn. Besides these, the deposition of alloys, the solution of alloys, the electrolysis of mixed electrolytes, the function of intermediate (bi-polar) electrodes, the exact *modus oper-*

*andi* of porous diaphragms, the relation of viscosity to electric conductivity and ionic mobility, the limitation of the speed of electrolysis by the diffusibility of the products, the solubility of metals in their own fused salts, the function of gases in solution, the compounds of solvent with solute and their relations to complex ions and the mechanism of electrolysis, are only some of the many phenomena whose investigation has only begun, and which lie invitingly before us. Professor A. A. Noyes has blazed a new trail by his systematic work on the electric conductivity of solutions at high temperatures, and Dr. Kahlenberg by his researches on the electrolysis of non-aqueous solutions. Let these advise us that there are as many new fields awaiting attack as there are old ones needing thorough exploration.

In the whole realm of pure science (meaning thereby the investigation and classification of phenomena) there is no field offering more attractions at the present moment, none more ripe for exploitation, none more promising of large rewards for honest work, than electrochemistry. The science is yet in its infancy; many of its pioneers are yet living (the original patentee of nickel plating contributes a paper to this very meeting), and the gates of opportunity are opened wide to every one of us to go do likewise—to become pioneers in our turn.

## II. THE BUILDING OF A COMPREHENSIVE ELECTROCHEMICAL THEORY.

In this respect we must confess at the outset that our science is in a state of transition. We know what we are abandoning, we hardly as yet grasp the newer theory to which we are groping our way. In the past plausible explanations have been advanced which fitted the known facts fairly well, only to be afterwards shattered by new facts which could not be made to fit into the theory. Scientific theories must enlarge to fit the new truth or be broken by it, and so our theories must be in a state of constant flux if the science to which they belong is a live, growing science, receiving continually accretions of new truth.

Not very long ago the burning electrochemical question was, 'Is the theory of electrolytic dissociation the true explanation of the nature of a solution?' I shall not say that it is not, because I do not know; but I am certain that the man is making a mistake, whoever he may be, who says that 'it is certainly true.' My own conception of the state of solution is that the solute is in an abnormal *physical* state, having resemblance to the gaseous state, and that in some cases a definite compound of the solute with the solvent exists in the solution, it also being in the abnormal physical state, but not abnormal chemically. The grounds for this view would take too long to explain, but they appear to me to point to this as an explanation more satisfactory than the assumption of an abnormal chemical condition of dissociation.

Large generalizations like the theory in question, however, are very seldom directly proven false; the evidence of their insufficiency simply accumulates until the conviction arises or grows in men's minds that something else explains the facts better, and the older theory thus fades into the background. At the present time the physical chemist, or perhaps rather the chemical physicist, has thrown so much light upon the structure of the atom by his discoveries regarding electrons that it appears as if a new and a very brilliant side-light is about to be thrown upon the subject of electrochemical phenomena. If it be true, as Professor J. J. Thomson has apparently just proved, that the arrangements of the elements in families according to the periodic law, their periodic increase and decrease in valence, and change from electropositive to electronegative character, can

be postulated as a necessary deduction from the hypothesis of the atoms consisting of uniform shells of positive electricity, inclosing negative electrons arranged in rotating rings, then the ionic conception will of necessity yield place in electrochemical science to the electronic. In this connection it ought to be noted that Professor Thomson's inferences as to what constitutes chemical combination, the electrically neutral atoms losing or gaining electrons and thus becoming positively or negatively electrified, and therefore attracting each other, agree with and supplement to a nicety the system of positive and negative bonds elaborated twenty-five years ago by our respected member, Professor O. C. Johnson.

The nature of the act of solution bears so fundamentally upon the mechanism of electrolysis that light thrown upon it from any direction is very welcome. Professor J. H. L. Vogt, of the University of Christiania, has recently published the first section of a work on the nature of fused silicates which bears so directly upon the question of fused baths, and particularly of the condition of compounds dissolved in fused baths, that the close study of his work will undoubtedly assist the electrochemist in understanding fused bath electrolysis and, in fact, the problem of solution in general. It is, indeed, the fact that many bases dissolved in fused silicates retain their chemical individuality, and can be proved to exist there simply in an abnormal physical condition. The analogous process in regard to solution in water passes current under the name of ionization, or electrolytic dissociation. From these and similar investigations the conviction is being pressed upon us that physical solution of one substance in another covers a large part of the field formerly supposed to be entirely chemical in its nature, and that the eutectic mixtures resulting are in no sense chemical compounds, but that the latter constitute nodes or critical points of the mixtures, while in between, in the ordinary run of solutions, we are dealing simply with these chemical compounds mutually dissolved in each other, and in no other states than abnormal *physical* states. The electrolysis of a substance in solution means usually, therefore, the decomposition of that chemical substance existing in an abnormal physical state, and not the act of gathering at the electrodes the ions of the previous dissociated chemical compound.

These are the personal views of your speaker, and are, of course, not put forward as necessarily representing those of any other member of this society. They are given here because I believe that the advance in electrochemical theory in the near future will be in this direction and along these lines.

III. APPLICATIONS TO INDUSTRIAL NEEDS.

If electrochemistry concerned itself only with the study of phenomena and their classification, the deduction of laws and the building of theories thereupon, it would satisfy one of the fundamental needs of the human mind, that of *knowing*, but would leave unsatisfied another and equally vital desire, that of *using*.

As one indication of this we see the program of our meeting classified into experimental, theoretical and industrial. (I stand convicted of having plagiarized the plan of the program in laying out the subjects of my address.) Without the latter item the electrochemical field would remain a thing apart from the sympathy of the world at large, and it is really by reason of the absorbing interest and great economic value of these industrial applications that we have with us the support and cooperation of the educated and the commercial world.

The various items in which, in industrial chemistry and metallurgy, electrochemical

methods have either superseded ordinary non-electric methods, or else have created new industries, form a catalogue sufficiently long to arrest the attention of the most superficial observer, and altogether too long to be mentioned in detail within the limits of this address. Suffice it to mention in passing the millions of dollars' worth of copper electrolytically refined, not annually, but monthly; the 100,000 horse-power consumed in producing calcium carbide; the reduction of the cost of aluminium from $5 a pound to 30 cents; of sodium in almost an identical ratio; the revolution being wrought in one of the largest chemical industries by the production of electrolytic alkali and bleach; the capturing of the potassium chlorate industry and the manufacture of phosphorus.

The whole story, if related at length, would be the old story of *homo sapiens* having discovered a new tool, a new instrument wherewith to torture mother nature; a new means of reaching old or of creating new results, and he is necessarily immersed in enthusiasm for this 'genius of the lamp,' which has performed so many wonders and promises so many more. For the use of electricity puts at our disposal temperatures never before industrially attained; gives us a decomposing agent at whose bidding the most powerful chemical compounds resolve into their constituents; enables us to attack and solve chemical problems in a manner before unthought of; opens up a world of possibilities whose scope we even yet but dimly comprehend. This is the fascination of the subject, the attractive force, the absorbing interest which is reflected in the enthusiasm of the electrochemist for his profession and in the gratifying success which has attended the formation and growth of this electrochemical society.

It remains to speak, with as much definiteness as the subject permits, of the possible enlargement and extension of these industrial applications. 'Whither' is a more important question than 'whence' when the present prosperity and future progress of the art are concerned.

Basing our remarks upon present developments, it may be perceived, to start with, that the electrical methods in chemistry and metallurgy which are most successful are either, *first,* those applied to the more powerful chemical compounds, whose decomposition by non-electric methods is highly difficult and expensive, or else impossible; or, *second,* those applied to new fields of very high temperature reactions impossible of attainment by other means, or, *third,* those applied to ordinary chemical processes, in which the directness of the electrical influence, be it decomposing, reducing or perducing, can not be duplicated or competed with by known non-electric methods.

Primitive man took his first lesson in metallurgy by learning to make iron; to this the ancients added lead, copper, silver, gold and even the volatile mercury. Many centuries later zinc was distilled, and only in the most recent times have sodium, aluminium and magnesium been possibilities. Painfully and slowly alchemy and modern chemistry toiled up the heights of the electrochemical series, from the easy conquest of the *noble* metals to the powerful mastery of the *strong* metals, and the steepest part of the ascent has been lightened by the aid of electricity, which has in many cases furnished the easy path to the conquest of the most difficult chemical problems.

It is related of our renowned geologist, Clarence King, that he was an enthusiastic mountain climber, and having from a distance spied a steep mountain, he conceived the ambition of conquering it. Taking a respite from surveying, he equipped himself for difficult climbing, and after several

hours of desperate effort finally stood on the summit of the seemingly impregnable butte, only to find an easy trail leading up on the other side.

The most abundant materials in nature are the fixed, difficultly transposable compounds of the strong metals, and their conquest and utilization are the peculiar and special province of electrochemistry.

According to the estimate of the indefatigable chemist of the Geological Survey, F. W. Clarke, silicon oxide forms 58.3 per cent. of the contents of the solid crust of the earth, aluminium oxide 14.7 per cent., iron oxide 7.8 per cent., calcium oxide 5.3 per cent. and magnesium oxide 4.5 per cent.; or, expressed in another way, silicon 27.2 per cent., aluminium 7.8 per cent., iron 5.5 per cent., calcium 3.8 per cent. and magnesium 2.7 per cent.

With these figures in mind, may I not ask whether we fully realize the significance of one of the latest electrometallurgical triumphs, the production of metallic silicon on a large scale in the electric furnace by one of our Niagara Falls members, Mr. F. J. Tone? While the catalogues of dealers in rare chemicals are still listing silicon at dollars an ounce, an electrochemist has two barrelfuls of it which he is wondering if any one will buy at a fraction of a dollar a pound! Could anything better illustrate the revolutionary character of electrochemistry? While the electrochemist is the reverse of a nihilist, we must admit that he is a typical and convicted revolutionist.

To say a word or two more about silicon. I had a somewhat uncanny feeling when Mr. Tone introduced me to his half a ton of silicon. "Here is," I soliloquized, "the first chance which mankind has had to utilize the most abundant solid element on earth. What will be made of it? Can it become as useful as iron? Probably not. Can applications be found for it which will bring it among the ordinary metals of every-day life? Possibly. In any event, here is the material, ready to hand, and no one but the electrochemist could have made it."

Something of the same feeling must have arisen in the mind of the chemist who first made aluminium a commercial possibility, but his expectations, based on his chemical process, were only actually realized when the electrochemist gave his solution of the problem. This very element illustrates one of the chief characteristics of electrochemical processes, viz., their potentiality for improvement. Chemically produced aluminium was out of the race when the metal sold for one dollar per pound, yet the present market price is only one third of that. After the chemical process has done its utmost, has said its last word, the electrochemical process, which supersedes it, has only *begun* its march of improvement.

In the metallurgy of iron, a direct replacement of the ordinary manufacture of pig iron by electrical processes is very far from a possibility, even in countries where coal is most expensive and water power most abundant. However, in the manufacture of that higher-priced product, steel, the case is different, and already some of the finer qualities, such as replace crucible steel, are being made electrically in France, Switzerland and Sweden. It is only a question of some more inevitable improvements being made in the electric furnaces used to make possible the manufacture in them of the more common and cheaper varieties of steel. This will come at first in countries where fuel is dear and power cheap, and afterwards in localities where very cheap power is being generated by gas-engines using either the waste gas from blast furnaces or producer gas made from coal waste or culm.

Even before that time the auxiliary use

of electric heating to take off the 'peak of the load,' so to speak, in our open-hearth steel furnaces—that is, to furnish the last few hundred degrees of necessary temperature while the combustion of gas furnishes the lower range—is a distinct commercial possibility. Already our steel works are a network of electrical appliances for running cranes, charging machines, hoists and cars, and the step is not a long one to employ this already-present agent to help the heating gases over the heaviest part of their work, the bringing up of the charge to tapping heat.

Next to iron in natural abundance is calcium, and our chemists and metallurgists are only beginning to appreciate its possibilities. Occurring as almost chemically-pure calcium carbonate, in inexhaustible quantities and at the cost of only a few cents a ton for quarrying, the question of producing the metal cheaply is the particular task of the electrochemist. The cost of the metal is practically the cost of its reduction, and there is no doubt that the electrometallurgist can and will solve this question as he has that of aluminium and silicon. Calcium is, at temperatures above a red heat, the strongest metallic base existing, and is therefore the most powerful pyrochemical reagent. By its use many problems may find their solution, such as the complete deoxidation of melted metals, the reduction of rare elements and many other interesting reactions.

Magnesium does not occur quite so plentifully as calcium, but still it is so common that 99 per cent. of the present cost of making magnesium must be charged against the process used and only 1 per cent. against the raw material. There is no reasonable doubt but that careful study put upon the electrolytic production of magnesium would result in its being produced at a fraction of its present cost. It is certainly a metal which, at its present price, has very limited uses, but, with a specific gravity of only 1.72, a capacity for being hardened and strengthened like aluminium and the property of forming valuable alloys with copper and with aluminium, it is certain that its cheap production would mean another metal added to those in everyday use.

There is yet another metal of kindred character worth considering. Beryllium occurs in the gem beryl as silicate of aluminium and beryllium. The mineral is found massive in large enough quantities to form a commercial source of the metal. The separation of the beryllium oxide from the silica and alumina is not a very difficult chemical operation, but could probably be simplified by the application of Hall's process of differential reduction in the electric furnace. The reduction of beryllium oxide to metal dissolved in a fused bath of alkaline and beryllium salt is a step which would probably yield to investigation, while the collecting of the metal floating upon the bath should offer no greater difficulties than does the collecting of sodium.

With a brilliant white color, specific gravity 1.6, malleable, ductile, forming fine alloys, there are a large number of possible applications for beryllium if it can be obtained cheaply, and it is to the electrochemist that we must look for the solution of this problem.

In the electrolytic refining of metals, copper was the first to yield commercial results, silver next, then gold, lead and bismuth. Yet there are others awaiting conquest. The electrolytic refining of nickel, zinc, antimony and tin has been attempted, but not yet commercially mastered; that of aluminium is an attractive question because of the economy it would produce. Instead of purifying by costly chemical methods four tons of aluminium ore, we have the alternative problem of refining one ton of impure aluminium, and with a large margin of difference in com-

mercial value to work upon. It may be, since electrolysis in aqueous solutions appears impracticable, that refining in non-aqueous solutions, or in easily fusible salts, would conquer the difficulty.

In the field of producing ferro-alloys of the rare metals, for use in making special steels, even the crude electric furnaces in present use have demonstrated their ability to produce these alloys at the minimum cost. Here is a field which has been practically occupied by electric-furnace methods, or by the Goldschmidt process, using electrolytically produced aluminium, and one does not need to be much of a specialist in chemistry or metallurgy to see the wide vista of commercial opportunities here opening before us.

While our largest electrometallurgical industry is that of copper refining, the largest industrial electrochemical operation is that of producing calcium carbide. Calcium carbide, a substance practically unknown to even the skilled chemist a few years ago, and now being produced by thousands of tons annually. Calcium carbide, the commercial key to the gateway first pointed out by Wöhler, when he made artificial urea.

But why only *calcium carbide?* This is only one of the numerous carbides first produced commercially by electrical methods. Silicon carbide is another which has found broad applications and formed a new industry, and it is not only possible, but most probable, that other metallic carbides may find large applications. Moissan has shown, for instance, that uranium carbide produces, with water, liquid hydrocarbons like petroleum, and the production of artificial petroleum is a scientific possibility, although not at present commercially practicable. Besides the carbides, there are other electric-furnace products—the metallic nitrides, which are awaiting further study and utilization.

One of the most vigorous and industrious electrochemists said to me once, "We are so overwhelmed by new things of possible use to science or industry that we can at most investigate only a small fraction of them. It is a virgin continent of undeveloped possibilities."

Of the possibilities of the direct preparation of metallic compounds from the metals, the transformation of metallic salts into other compounds, the fixation of the nitrogen of the air, the increased application of the simple, direct and elegant methods of electrolytic decomposition, reduction or perduction in organic chemistry, the electrification of soils and its influence on agriculture, the sterilization of water by electrically made ozone and the disinfection of sewage and their contribution to sanitary science, and the various other unmentioned possibilities of electrochemistry, time literally fails in a simple endeavor to mention, let alone to discuss them.

The great services which electrochemistry has rendered humanity, and the march of civilization in the past decades which measure its brief but phenomenal advance, are but a fraction and an earnest of what is yet to be accomplished. If in the battle of industrial competition you are summoned by the conservatives of industry to strike your colors, answer with the courage and determination of the intrepid Captain John Paul Jones, 'Surrender, sir! We have only begun to fight.'

Joseph W. Richards.
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## *DISTRIBUTION OF INDIAN TRIBES IN THE SOUTHERN SIERRA AND ADJACENT PARTS OF THE SAN JOAQUIN VALLEY, CALIFORNIA.*

The distribution of Indian tribes in California has never been completely worked out. This is due partly to the difficulty of the undertaking but mainly to the inadequate amount of field work thus far